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PRELIMINARY CHARACTERIZATION OF MATERIALS FOR A REACTIVE TRANSPORT MODEL VALIDATION EXPERIMENT

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ABSTRACT

The geochemical properties of a porous sand and several tracers (Ni, Br, and Li) have been characterized for use in a caisson experiment designed to validate sorption models used in models of reactive transport. The surfaces of the sand grains have been examined by a combination of techniques including potentiometric titration, acid leaching, optical microscopy, and scanning electron microscopy with energy-dispersive spectroscopy. The surface studies indicate the presence of small amounts of carbonate, kaolinite and iron-oxyhydroxides. Adsorption of nickel, lithium and bromide by the sand was measured using batch techniques. Bromide was not sorbed by the sand. A linear (K_d) or an isotherm sorption model may adequately describe transport of Li; however, a model describing the changes of pH and the concentrations of other solution species as a function of time and position within the caisson and the concomitant effects on Ni sorption may be required for accurate predictions of nickel transport.

I. INTRODUCTION

Models used in performance assessment and site characterization activities related to nuclear waste disposal rely on simplified representations of solute/rock interactions, hydrologic flow fields and the material properties of the rock layers surrounding the repository. A crucial element in the design of these models is the validity of these simplifying assumptions. An intermediate-scale experiment is being carried out by Los Alamos National Laboratory and Sandia National Laboratories for the Yucca Mountain Site Characterization Project to demonstrate a strategy to validate key geochemical and hydrological assumptions in performance assessment models. The overall objectives and plan for the experiment are described in Siegel et al.[1]

The experiment involves the detection and prediction of the migration of fluid and tracers through a 6-m high x 3-m diameter caisson filled with a porous medium. An overview of the mechanical design of the caisson, characterization of the hydraulic properties of the porous medium and a description of transport calculations used in the design are given in a companion paper[2]. This paper describes the geochemical characterization of the porous medium and tracers that was carried out as part of the design phase[1] of the experiment.

The caisson is filled with Wedron 510 sand, a commercially available silica sand, (Wedron Silica, Wedron Ill. 60557). According to its bulk chemistry and mineralogy, Wedron 510 sand is nearly pure quartz, but preliminary characterization[3] suggested that it contains at least three other chemically reactive components: carbonate, iron oxyhydroxide, and kaolinite. Of particular interest at this stage of the work are several questions related to the nature of these minor phases: 1. What role do they play in the overall sorption behavior of the sand? 2. Are the minor phases present as surface coatings or discrete mineral grains? 3. What will be the effects of dissolution of the quartz and the minor minerals on the chemical compositions of the pore water and mineral surfaces and on the behavior of the tracers.

As discussed in Siegel et al.[1] a suite of reactive tracers that spans a variety of chemical behaviors was considered for the caisson experiment. The tracers that were chosen for the final design include: 1. bromide, a conservative tracer that can be used to track the movement of water in the caisson, 2. lithium, a tracer that forms relatively weak surface complexes, and 3. nickel, a transition metal that forms strong surface complexes with geologic materials and is representative of waste elements released from the structural materials in the high-level waste. For the purpose of caisson design, experiments were conducted to examine the most important influences on sorption for each tracer. Based on a review of the literature[4,5,6,7,8] and preliminary experiments[1], the it was proposed that sorption of lithium by the sand would be influenced by tracer concentration and that sorption of Ni would be sensitive to solution pH. Data describing these relationships are described in this paper. In addition, interactions between the tracers and solution sampling equipment were studied to estimate the associated uncertainties in measurements of the time-dependent tracer concentration profiles within the caisson.

The formulation of a framework for data collection that supports the long-term objectives of the caisson experiment (ie. the validation of geochemical approximations used in models of reactive transport) also is described in this paper. Three major issues that are being addressed to develop the framework are: 1. What geochemical characteristics of the porous medium will dominate chemical retardation of tracers? 2. What are the primary contributors to the uncertainty in the accurate detection of the tracers in the caisson? and 3. Which geochemical models adequately describe tracer migration? For the detailed characterization phase of the caisson experiment[1], a more complete set of data, describing the interactions between each tracer and the sand, among the tracers, and among the tracers and the other solutes in the pore water of the sand is being collected in such a way as to allow application of several models of geochemical retardation.

II. METHODS

A. Mineralogical Analysis

The mineralogy of the Wedron 510 sand was characterized by powder X-ray difraction with a Scintag diffractometer. Morphoplogies of sand grains and surface coatings were examined by petrographic microscope and scanning electron microscopy with energy dispersive analysis. The surface area was measured with the BET (Brunauer, Emmett, and Teller) method.

B. Bulk Composition and Surface Leaching

A homogeneous ~100 g sample of Wedron 510 sand was obtained by a splitter, loaded into a sieve stack and placed on a Pulverit Vibrator. Chemical analyses of bulk compositions and surface coatings were made of several particle size fractions. The subsample for bulk analysis were digested in HF and HNO_3, spiked with Be, Sc, and In to act as internal standards for mass spectrometric analysis and then taken up in 100 m*l* 1% nitric acid solution. Surface coatings were assumed to be represented by components leachable in boiling 6 *N* HCl. After boiling the sand, the leachate was evaporated to dryness, redissolved in a few m*l* 1% nitric acid solution, filtered through Whatman #42 filter paper, spiked with Be, Sc, and In, and diluted to 100 m*l* with 1% nitric acid. Both sets of samples were analyzed for major and minor elements on the VG Instruments Plasmaquad ICP-MS (Inductively-coupled-plasma mass spectrometer). For Ca and Si analysis, 50 m*l* of the sample solutions was evaporated to dryness, taken up in a few m*l* of deionized (D.I.) water, and analyzed by atomic absorption (AA).

C. Unsaturated Column Leaching Experiments

Small-scale column experiments were carried out to study the changes in the pH and composition of leachable components of Wedron 510 sand in dilute NaCl electrolyte as functions of time and saturation state. A schematic of the column apparatus is shown in Figure 1. NaCl solutions (0.01 *M* or 0.001 *M* NaCl, pH $\cong$ 6) were pumped through columns (7 cm I.D. x 24 cm) filled with Wedron 510 sand. The pore volume of the column was approximately 180 m*l*. The flow rate and bottom boundary suction was varied to control the degree of saturation (50% - 100%). The pH of the influent solution was measured in a top reservoir and also in a flow-through cell just prior to entry into the column. The pH of the effluent solution was measured in a flow-through cell as it exits the column and after it was collected in an open vessel. In experiments with 0.001 *M* NaCl influent, samples of effluent were acidified (1% HNO_3) and analyzed for Al, Ca, Mg, Li, Ni, and Br by ICP-MS. Si was determined for each sample by atomic absorption.

D. Potentiometric Surface Titrations

Acidimetric-alkalimetric titration curves for Wedron 510 sand and Min-U-Sil 5, a reference α-quartz from the Pennsylvania Glass Corp. (Pittsburgh, PA), were obtained over the pH range 2.65 to 10 at increments of ~1 pH unit. Aliquots of 49 m*M* HCl and 37 m*M* NaOH were added to batch systems consisting of 20 m*l* 0.01 *M* NaCl electrolyte and 15 g sand in 40 m*l* polyallomar (PA) centrifuge tubes. Periodic pH measurements were made at intervals of 0, 3.0, 5.8, and 31 days. CO_2-free conditions were maintained by preparing solutions from boiled deionized water, purging the headspace of all vessels with Ar and carrying out pH measurements under Ar purge.

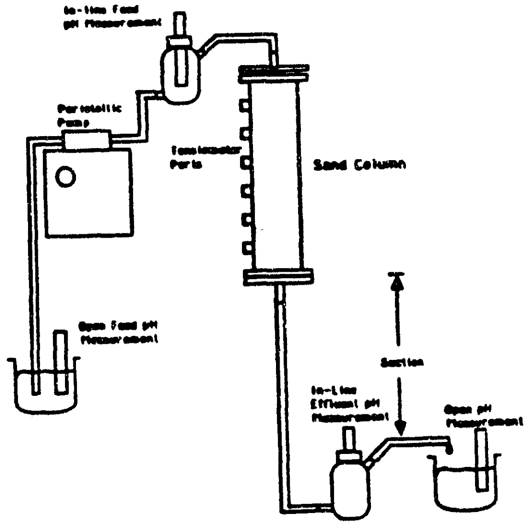

Figure 1. Experimental Apparatus for Unsaturated Flow Sand Column Leaching Studies.

To evaluate the effects of mineral surface coatings, titration curves were obtained on the sand and Min-U-Sil 5 in both raw and surface-cleaned states. Surface coatings were removed from the Wedron sand and the Min-U-Sil 5 using a cleaning procedure adapted from Kohler and Leckie[4]. The sample was ignited to remove organics, refluxed in $HClO_4$ to remove soluble cations, washed in dilute NaOH to neutralize the acid, thoroughly rinsed, and finally dried. Batch systems contained 20 m*l* electrolyte and a sorbent surface area of 3.15 m^2 (either 15 g sand or 0.53 g silica).

E. Batch Sorption Experiments

Ni sorption was measured in batch experiments at solid:solution ratios of approximately 1:1 over the pH range 5 to 9.5. Ni tracers were prepared from Fisher Ni AA Standard (1000 μg/m*l* in 2% HNO_3). The experiments were carried out under atmospheric or CO_2-free conditions in 0.01 or 0.001 *M* NaCl in 40 m*l* polycarbonate (PC) or PA centrifuge tubes. Initial Ni concentrations were 50 or 100 ng/g and 15 or 20 g of sand were used. The sand and electrolyte were pre-equilibrated for 48 - 72 hr and then equilibrated for 18 to 48 hr after addition of the tracer on a hematology mixer. After this period, the samples were centrifuged for 10 minutes at 11,000 rpm and allowed to cool to room temperature. The pH of each sample was measured using an Orion Research Model 940 pH meter as described below. Approximately 15 m*l* of the supernatant was removed from the centrifuge tube, passed through a 0.2 μm nylon filter attached to a plastic syringe and placed directly into 7 m*l* polyethylene vials. Final Ni concentrations were measured by graphite furnace atomic absorption (GFAA) spectroscopy as described below.

Batch studies of sorption of lithium and bromide by Weldron 510 sand in 0.001 *M* NaCl under atmospheric conditions were carried out in 40 m*l* PC centrifuge tubes. Reagent grade lithium bromide (LiBr) was used as the source for both lithium and bromine. Solution:sand ratios of approximately 1:1, 5:1, and 10:1, and lithium and bromine concentrations of 1.44×10^{-5}, 1.44×10^{-4} and $1.44 \times 10^{-3}\,M$ were used. The samples were allowed to pre-equilibrate for approximately six days and to equilibrate for approximately seven days after tracer addition while being continuously stirred on a hematology mixer. Solution-solid separation procedures were the same as those described above. The samples were then analyzed for lithium by atomic adsorption and for bromine by ion-specific electrode as described below.

F. Ni Solubility Studies

Ni solubility studies were carried out under CO_2-free conditions in 30 m*l* 0.001 *M* NaCl electrolyte over the pH range 5 – 10 in 40 m*l* PA centrifuge tubes. In an effort to provide nucleation sites for precipitation of $Ni(OH)_2$, ~ 1 m*l* of a neutral 200 ng/m*l* Ni solution was first evaporated in each tube. Next, 30 m*l* of electrolyte was added and then enough Ni was added to provide an initial concentration of $<10^{-2}\,M$ for systems with target pH < 8, or an initial concentration of $10^{-4.77}\,M$ for more alkaline systems. In the alkaline systems, Ni was added as 1000 μg/m*l* Ni solution in 2% HNO_3; in the acidic systems, Ni was added as $NiCl_2{*}6H_2O$ solid. Weak NaOH and HNO_3 solutions were used to adjust the pH of each tube to its target value (± 0.1 pH units). The systems were nominally $10^{-3}\,M$ NaCl ($I = 0.001\,M$), but became significantly stronger for those at low pH because of the addition of large amounts of $NiCl_2{*}6H_2O$, reaching $I \sim 0.03\,M$ at pH 5.4.

After static storage for two days, the tubes were placed on hematology mixers and gently agitated for eight days. At the end of this period, pH was measured and aliquots pipetted for Ni analysis. Each aliquot was filtered as described above for sorption studies and Ni concentrations were determined by GFAA as described below.

G. Chemical Analyses

Nickel concentrations were determined using graphite-furnace atomic absorption spectroscopy (GFAA) on a Perkin-Elmer HGA-5000 with a graphite-furnace programmer and an auto-sampler. The data-reduction scheme applies a quadratic fit to the absorbance data and corrects for evaporation from the auto-sampler vials to achieve better than 1.8% precision over a dynamic range of 0 – 200 ng/m*l*, with a limit of detection of 0.2 ng/m*l* or better.

Lithium analyses were obtained using air-acetylene flame atomic absorption (AA) spectrophotometry on the Perkin-Elmer HGA-5000. The samples were drawn directly from the polyethylene vials at approximately 4.1 ml/min. A calibration curve was derived from a quadratic fit to the absorbance data using measurements made on blanks (0.001 *M* NaCl electrolyte) and standards of 1 μg/m*l*, 5 μg/m*l*, and 10 μg/m*l* Li.

Br was analyzed with an ORION 94300 Br ion specific electrode with a ORION 900100 single junction reference electrode. pH measurements were made with an Orion ROSS #8104 combination electrode connected to an Orion 940 pH meter. The electrode was calibrated against pH 4, 7, and 10 buffers (actual values entered in the meter were corrected to the ambient temperature) using the Orion's internal 3-point calibration routine. Internal precision of the pH calibration is ± 0.03 pH units.

Measurements of pH were made under CO_2-free conditions in order to reduce the confounding influence of disequilibrium with atmospheric CO_2. A low-flow Ar purge system with a two-stage scrubber purged the headspace of the batch-experiment containers during pH measurements and maintained CO_2-free conditions. The first scrubber was filled with 0.5 M NaOH to remove an acidic contaminant in the Ar (probably CO_2 or HCl); the second stage contained boiled deionized water to remove NaOH aerosol. In the Ni solubility studies pH readings were taken after allowing the electrode to stabilize for 4 minutes.

Major and minor elements in leachates from batch and column studies were analysed on a VG Instruments Plasmaquad ICP-MS. An aliqout of each sample was spiked with 1000 ng/m*l* each of Be, Sc, and In, and run along with prepared standards, which defined the calibration curve. The standards were run again as unknowns to determine the detection limits and errors for each element.

III. RESULTS

A. Mineralogical Studies

The bulk mineralogy of the sand was determined by X-ray diffraction; the patterns show significant diffraction maxima for quartz only. A detailed examination of the XRD pattern for minor peaks between 6° and 64° fails to reveal any sign of carbonate, but shows traces of kaolinite as well as four unidentified peaks. A colloidal fraction of the sand (0.05% by weight) which remains dispersed at pH > 8.5 was also analyzed by XRD. It shows clear diffraction maxima for quartz and kaolinite, and again lacks any sign of carbonate. Observations using SEM revealed a collection of ragged fragments whose EDS spectra were dominated by subequal intensities of Al and Si X-rays with lower intensity (usually) of O X-rays. No fragments of quartz were observed, implying that quartz constitutes probably no more than 10% of the colloidal fraction. Studies of thin-sections under an optical microscope reveal that the sand grains are coated with a yellowish material suggesting that Fe is likely to be present as a thin coating of hematite and/or goethite on the sand grains.

B. Bulk Composition and Surface Leaching Experiments

The size analysis of the Wedron 510 sand obtained by dry sieving is shown in Table 1.

Table 1. Sieve results for Wedron 510 sand

U.S. sieve #	Size fraction	Weight % of total
50	fr. > 295 µm	8.91
70	295 µm > fr. > 212 µm	39.55
100	212 µm > fr. > 150 µm	27.74
140	150 µm > fr. > 106 µm	16.63
200	106 µm > fr. > 74 µm	6.42
Pan	74 µm > fr.	0.75

Chemical analyses of the bulk chemical samples (dissolvable in concentrated HF and $HClO_4$) and surface leachates (dissolvable in hot 6 *N* HCl) from an unsieved sample and two particle size fractions are shown in Table 2. Surface concentrations are expressed as the mass of the element in the leachate divided by the weight of the sand sample. No values are given for Br in the surface chemistry samples because the Br contamination from the HCl was too high. Values of Si concentration are close to 100 wt.%. The composition of the 212 µm-150 µm fraction was similar to that of the 295 µm - 212 µm fraction shown in the table. The bulk analyses of the finer size fractions that are not tabulated (150 µm-106 µm and 106 µm-74 µm) were more enriched in all of the minor and trace metals compared to the coarser fractions.

Table 2. Chemical analysis of Wedron 510 sand*

	Size Fraction					
	unsplit sand		295µm - 212µm		< 74µm	
Element	bulk	surf	bulk	surf.	bulk	surf
Li	1.54	0.05	1.70	0.06	2.47	0.06
Na	1.67	<0.20	1.00	<0.20	9.59	0.86
Mg	24.7	10.92	23.0	13.7	118	84.6
Al	2820	482	2290	579	11300	1200
Si	**	5.4	**	5.4	**	18.4
[illegible]	2.52	0.51	1.40	<0.20	20.1	1.10
Ca	55	23	46	26	222	198
Ti	83.1	2.55	61.1	2.35	892	13.2
Fe	242	80.0	128	39.0	2280	1180
Ni	0.18	0.14	0.09	0.09	2.08	0.90
Br	1.68	***	0.34	***	<0.75	***

*Values in µg/g; ** SiO_2 content was ≅100%; *** analyses not reliable due to contamination.

The bulk analysis of the finest size fraction and the surface coatings of all size fractions contain high concentrations of Al, Fe Ca, and Mg. This suggests that the finest size fraction contains fragments of sand grain coatings composed of calcite, dolomite, iron oxyhydroxide and clay minerals. Table 3 tabulates the fractions of total element mass contained in the surface coating and indicates that the surface coatings contain significant fractions of the Mg, Ca, Fe and Ni in all size fractions.

Table 3. Ratios of Surface/Bulk Concentrations

Element	Size Fraction		
	unsplit sand	295μm > fr > 212μm	< 74μm
Li	0.03	0.03	0.02
Na	0.12	0.20	0.09
Mg	*0.44*	*0.59*	*0.72*
Al	0.17	0.25	0.11
K	0.20	0.14	0.05
Ca	*0.42*	*0.57*	*0.89*
Ti	0.03	0.04	0.01
Mn	*0.33*	*0..21*	*1.46*
Fe	*0.33*	*0.30*	*0.52*
Ni	0.78	0.92	0.43

C. Unsaturated Column Leaching Experiments

The results of the unsaturated leaching experiments are shown in Figure 2. The column effluent contains measurable concentrations of the major components of the sand (Ca, Mg, Si) and of the tracers (Ni, Br, Li) that will be used in the caisson experiment. The initial spike in the concentrations may be due to transient increase in the level of saturation during elution of the first 3 pore volumes; the concentration appeared to approach a steady state thereafter.

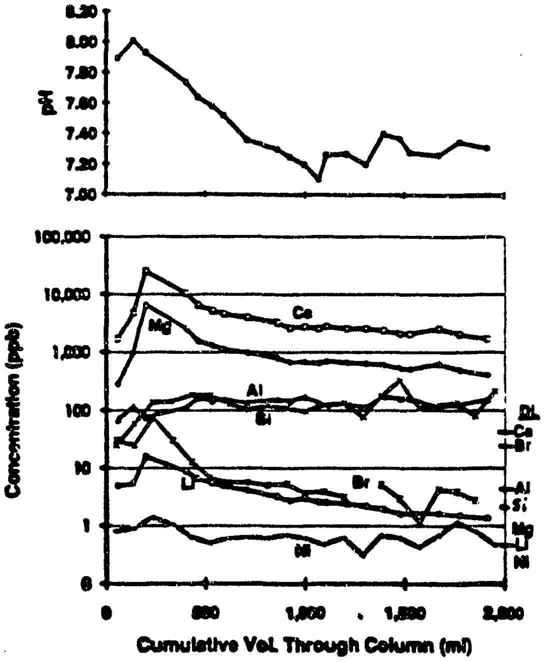

Figure 2. pH and Compositions of Effluent Samples from Unsaturated Flow Sand Column Leaching Experiments. Estimated detection limits for the ICP-MS are shown on the right axis of Figure 2.

Under unsaturated conditions the effluent pH dropped to a steady-state range of 7.2 to 7.5 after elution of approximately 5 pore volumes. In preliminary saturated-condition experiments (not shown), the pH of the effluent was initially neutral, rose to > 8.7, and then reached a steady-state value of approximately

8.2 after 6 pore volumes (approximately 1*l*) had been eluted from the column.

D. Potentiometric Surface Titrations

Titration curves for Wedron 510 sand at intervals of 0, 3.0, 5.8, and 31 days over the pH range 2.65 to 10 are shown in Figure 3. Readings at low pH (< 4) became less acidic by ~1.5 pH units within the first three days and then were stable. Readings at pH > 9 continued to drift with time, and near-neutral pH readings revealed the development of a buffering plateau. The pH shifts for pH < 9 are consistent with the dissolution of the conjugate base of a weak acid. Assuming the base to be carbonate-bearing minerals, a material-balance calculation for the most acidic batch system provides an estimate of the minimum carbonate content of the sand. The observed shift between 0 and 3 days of pH 2.76 to 4.33 requires an alkalinity of 1.93 µeq/g sand, corresponding to 0.96 µmoles/g of carbonate. All of the observed change in pH is attributed to carbonate dissolution, but some dissolution may have occurred after acidification but before the initial pH measurement.

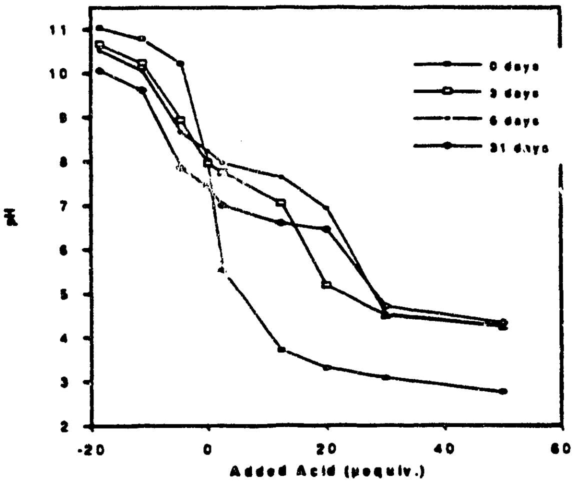

Figure 3. Potentiometric Titration of Wedron 510 Sand Under CO_2-free Conditions

Titration curves for acid-washed sand and acid-washed Min-U-Sil 5 silica show no time dependence except at very high pH (>10). In Figure 4, titration curves for these two systems are compared to the 31 day titration curve for unwashed Wedron 510 sand and to theoretical and experimental curves for 0.001 *M* NaCl electrolyte alone. The model titration curve for the electrolyte was adjusted to pass through the experimental data points at low pH. Titration curves for both acid-washed materials are essentially identical, confirming the efficacy of the acid-washing procedure, and suggesting that the sand is composed of quartz armored by acid-soluble phases.

At low pH, the acid-washed curves are coincident with that for electrolyte alone. This is expected because the pH of the zero-point-of-charge (pH_{ZPC}) of quartz is ~2; therefore, at low pH, the quartz surface is mostly un-ionized. In deionized water (at 0 µequivalents added acid) surface ionization is significant, contributing H^+ to the solution and hence reducing the pH from neutral to ~5.2 in both sand and silica systems. Under basic conditions, the titration curves fall well below that for electrolyte alone due to the combined effects of silica dissolution and surface ionization. At high pH, the titration curve for raw sand lies above its acid-washed counterpart, indicating that the quartz-grain surfaces are armored with phases that are comparatively insoluble at high pH, preventing equilibration between quartz and dissolved silica during the course of the experiment.

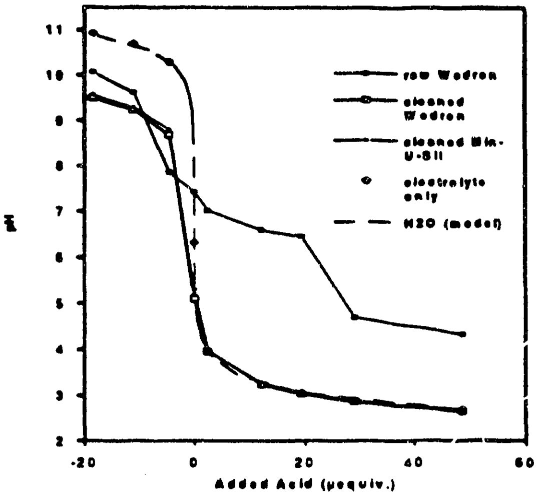

Figure 4. Potentiometric Titration of Raw and Acid-washed Wedron 510 Sand, acid-washed Min-U-Sil 5 Silica, and 0.001 *M* NaCl Electrolyte Under CO_2-free Conditions

E. Batch Sorption Experiments

Ni sorption (expressed as % sorbed) measured for the untreated sand at two solution:solid ratios over the pH range 5 to 10 are shown in Figure 5. The data show a sorption edge near pH 6.5 to 7, with measurable quantities remaining in solution even at the sorption maximum of 98% near pH 8. Because of the differing solid:solution ratios, the two data sets shown do not match up well in the region of overlap, at sorption values of 50-70%. The equivalent Kd's over the pH range of interest are 30 ml/gm (at pH = 7.2) to 80 (at pH = 8). A complicating factor that has not been fully quantified is the presence of leachable Ni in the sand at different pH's.

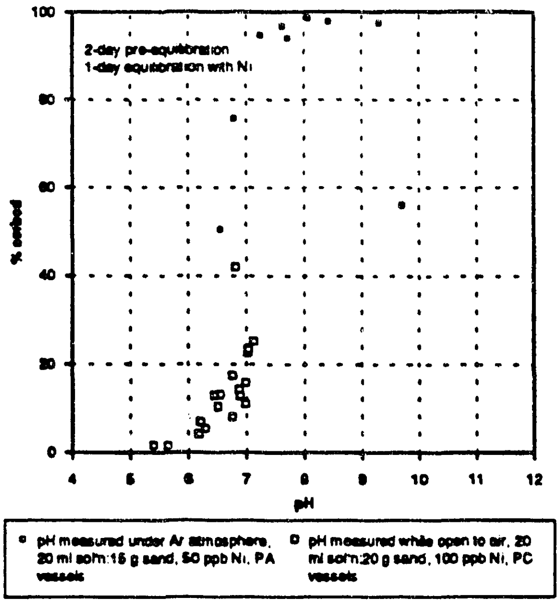

Figure 5. Nickel Sorption onto Wedron 510 Sand in Batch Systems.

Bromide sorption by sand was negligible over the pH range studied. Data from lithium sorption measurements are summarized in Table 3 and show that the K_d depends on both the tracer concentration and the solution:solid ratio. Preliminary attempts to fit the data to a Langmuir isotherm using a least squares analysis showed that the relationship between sorption and tracer concentration was different for each solution:solid ratio. Deviations of the experimental observations from calculated Langmuir isotherm plots were unacceptably large at the two higher solution:solid ratios. Additional data and analysis are required to determine if the Langmuir or another nonlinear isotherm is appropriate for lithium sorption by the sand.

Table 4. Summary of Lithium K_d's (ml/gm)

	Solution/Solid Ratio (ml/g)					
Total Li (µg/ml)	1		5		10	
	ave	σ	ave	σ	ave	σ
0.10	13	2.2	37	7.3	18	4.7
1	0.16	0.15	0.80	0.08	0.89	0.05
10	0.20	0.01	0.18	0.13	0.46	0.17

F. Ni Solubility Studies

Experimental solubility data obtained after 10 days of equilibration are compared with the published theoretical solubility vs. pH curve of Baes and Mesmer[5] in Figure 6. Analytical uncertainties are not shown, but are believed to be less than ± 0.15 pH units and less than ± 0.02 log units in Ni concentration, except for Ni < 10^{-7} *M*, where the uncertainty reaches +0.1/-0.2 log units. Batch systems plotting on the undersaturated side of the curve showed essentially no change in Ni concentration during the ten-day equilibration period. Batch systems plotting in the supersaturated field show significant decreases in Ni concentration over the same period, the magnitude of which appears to be related to the degree of supersaturation. Equilibrium is most closely approached at high pH; in fact, the datum at pH 9.9 may actually lie much closer to the curve. The Ni concentration here approaches the limit of detection of the GFAA technique, and so is subject to comparatively large uncertainty. The data are consistent with the published curve, and suggest that the kinetics of $Ni(OH)_2$ precipitation are moderately slow — ten days were insufficient to achieve equilibrium for small degrees of oversaturation.

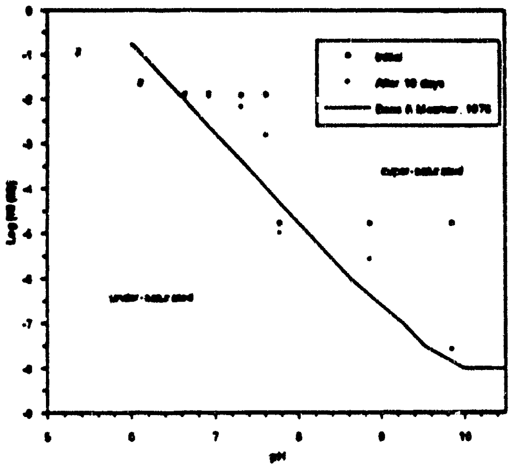

Figure 6. Ni Solubility under CO_2-free Conditions as a Function of pH.

G. Sorption of Tracers by Plastic Labware and Solution Samplers

Studies of tracer migration in the caisson and systematic laboratory studies of adsorption of tracers by sand will rely primarily on measurements of the concentration of the tracers in solutions. Direct measurements of the concentrations of tracers adsorbed to the solids will not be made routinely; therefore, any adsorption of the tracers by solution samplers or plastic labware must be accounted for in calculations of sorption partition coefficients (K_d's, isotherm parameters or surface complexation constants) or retardation factors. Appendix A describes studies of the adsorption of Ni as a function of pH by several kinds of labware used for sample collection tubes, syringes and centrifuge tubes. These include low-density polyethylene (LDPE), polypropylene (PP), polyallomar (PA), and polycarbonate (PC). The results indicate that each of the plastics becomes a significant sorber of Ni under neutral and alkaline conditions; this effect will have to be accounted for in sorption and solubility experiments. These studies also indicate that all of the plastics are suitable for use as geochemical sampling vessels for acidified solutions.

Uptake of tracers by the solution samplers will also introduce errors in estimation of breakthrough times in the caisson. Appendix A describes studies of the adsorption of the tracers by hollow fiber and ceramic samplers in static and flowing systems. The results indicate that the hollow fiber samplers do not adsorb any of the tracers but that the ceramic samplers will adsorb Ni and may be sources for Li and Br. At least 1 *l* of solution must pass through the sampler before the Ni concentrations of the influent and effluent become equal.

IV. DISCUSSION

Validation of contaminant transpor models involves comparison of calculated and observed tracer elution curves. The agreement between model predictions and experimental data will not be perfect because of uncertainties in tracer detection and the accuracy of model assumptions. Criteria for acceptable agreement must be formulated as part of a model validation test and must reflect various sources of uncertainty in the experimental and model designs. The caisson experiment described in this and related reports[1,2,3] was designed to provide well-controlled conditions and a well-characterized geomedia to allow separation of uncertainties due to chemical and physical processes.

The Wedron 510 sand was chosen for the porous matrix, because compared to other natural materials, it is relatively chemically and physically homogeneous. The physical properties of the sand are described in a companion paper. Detailed characterization of its geochemical properties, however, revealed that the sand is a mixture of several reactive phases. It is likely that chemical reactions involving the surfaces of the minerals, solutes in the pore fluids, atmospheric gases, the tracers, and the solution samplers will introduce uncertainties into the interpretation of the observed tracer breakthrough curves. The objective of the materials characterization studies is to obtain sufficent data describing these interactions to allow for comparison of the robustness of several different transport models with respect to this uncertainty. In this section the sources of uncertainty and the alternative geochemical models are described.

A. Uncertainty in Prediction of Chemical Conditions in the Caisson and Tracer Sorption

The leaching tests described previously indicate that significant amounts of the Li, Ni and Br will not be leached from the sand and interfere with the tracer tests. The studies also indicate, however, that the sand will not be chemically inert during the caisson experiment. Detectable amounts of Ca, Mg, Si were observed in both batch and flowing systems at low and near neutral pH. Significant pH shifts were observed and were dependent on the degree of hydraulic saturation in the flowing systems. The surface titration curves shown in Figures 3 and 4 indicate that the sand contains minerals whose slow dissolution will affect the solution pH. The existence of other potentially reactive minor minerals was indicated by analysis by x-ray diffraction, petrographic microscopy and scanning electron microscopy.

The available geochemical and mineralogical data suggest that the chemical composition of pore fluids within the caisson will be controlled by dissolution of quartz, carbonate cement, diffusion of atmospheric CO_2 into pore fluids, hydrolysis of silanol (SiOH) groups and hydrolysis of FeOOH surface groups (see Figure 7). It is anticipated that chemical conditions within the caisson will initially be transient but that a steady-state chemical profile may eventually develop. The flow velocity the dissolution rate of carbonate cement and the CO_2 diffusion rate will control the approach to steady-state pH profiles in the caisson: the amount of carbonate cement will determine the lifetime of the steady-state profile.

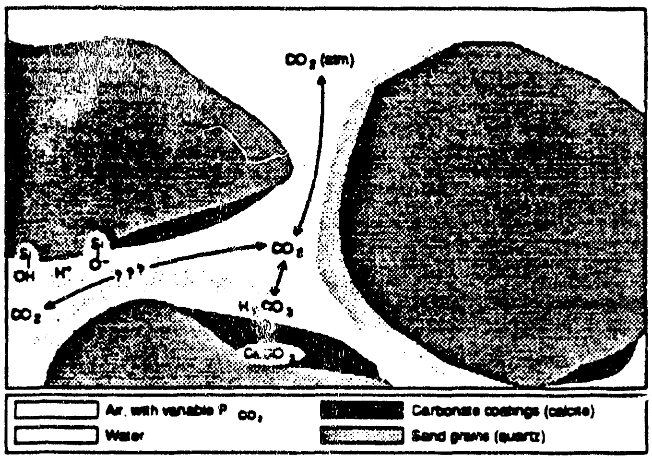

Figure 7. Factors Potentially Affecting pH in a Column Filled With Wedron 510 Sand.

Adsorption of solutes by mineral surfaces can potentially be affected by many properties of the adsorbent and adsorbate including: the surface area and charge of the adsorbent, the speciation and concentration of the adsorbate, and competition for sorption sites between the adsorbate and other solutes. As discussed previously, the pH_{ZPC} of quartz is ≅ 2; under the near-neutral conditions of the caisson, the surface of the sand should be negatively charged. Bromine is present in natural waters as Br^- and should not be adsorbed by the sand; this was confirmed by the sorption experiments described above. Thus, bromine should behave as conservative tracer; uncertainties in its elution curve should be attributed to hydrological effects.

Lithium is present in natural waters as Li^{2+}, a simple cation[5]; therefore, adsorption by the sand at near-neutral pH should be sensitive primarily to the surface area of the adsorbent, competition with other cations for sorption sites, and Li concentration. The data described in Table 3 indicate that Li sorption is nonlinear (ie K_d is a function of Li concentration and solution:solid ratio) but that over the range of interest (1-10 μg/l Li; 1:1 ml/g) sorption is low and fairly constant (K_d ≅ 0.2 ml/g). Thus, the contribution of geochemical effects to the uncertainty in the lithium breakthrough should be small and could be minimized by use of the appropriate nonlinear (isotherm) model for sorption.

The chemical speciation of Ni is considerably more complex than that of lithium or bromine because it forms complexes[6] with OH^- and CO_3^{2-}. Figure 5 indicates that Ni sorption by Wedron 510 sand is very sensitive to pH (or OH^- concentration) under near-neutral conditions. The results of the column experiments suggest that the pH in the caisson could be as high as approximately 8.2 and as low as 7.2. Figure 5 shows that nickel sorption ranged from about 20% to almost 100% for experiments with solution:solid ratios of about 1:1 ml/g. The corresponding range in calculated K_d is 15 - 90 ml/g. The uncertainty in tracer retardation factor is nearly proportional to the K_d, therefore, the error in our prediction of breakthrough times for Ni due to the unceratinty in pH could be as much as 600%. In the unsaturated caisson, the solution/solid ratio will be less than that of the batch sorption experiments (<0.2[1,2]); the associated error in the predicted Ni retardation factor for the caisson is not known at this time.

Figure 6 indicates that the solubility of Ni may vary by three orders of magnitude (approximately 10^{-5} - 10^{-2} M or 0.6 - 600 µg/ml) under CO_2-free conditions over the pH range relevant to the caisson. Preliminary speciation calculations indicate that the presence of CO_2 will not appreciably affect Ni solubility in the caisson. The use of low tracer concentrations (100 ng/ml) should prevent precipitation of $Ni(OH)_2$ in the caisson and in sorption experiments. Additional long-term solubility experiments are being carried out to obtain data at equilibrium.

B. Evaluation of Alternative Models for Sorption

The abilities of several different models of equilibrium sorption to predict transport of the tracers in the caisson are being examined. In order of increasing complexity and robustness they are:

1. Linear Sorption (distribution constant or K_d),
2. Non-linear sorption (Langmuir and other isotherms),
3. Ion exchange, and
4. Triple-layer surface complexation models.

The simplest model (linear sorption) requires a single constant (K_d) that is valid only for the physicochemical conditions of a particular experiment. In contrast, the triple-layer model (TLM) requires several adjustable parameters describing surface complexation of cations and anions, surface hydrolysis, electrostatic properties of the mineral surface double layer, and the density of surface sites[7]. The complexation constants are valid over a wider range of conditions than K_d's, however, considerably more experimental data must be gathered to obtain values for the adjustable parameters. Current high-level waste performance assessment codes use either K_d's or simple isotherms to represent retardation. These models are not structurally valid, ie. they do not accurately describe retardation mechanisms. However, if they can be shown to be predictively valid in the appropriate experimental frames (ie. predict the results of new experiments under relevant physicochemical conditions), then they can be used in performance assessment calculations.

C. Future Work

The dependencies of the lithium K_d on the concentrations of the tracer and the solids suggest that an isotherm sorption model may be required to predict Li transport. Additional data describing these relationships will be obtained to allow comparison of the vailidity of the Freundlich, Langmuir and other isotherm models for lithium transport. The data for Ni sorption, suggest that a model describing the changes of pH and the concentrations of other solution species as a function of time and position within the caisson and the concomitant effects on Ni sorption may be required for accurate predictions of nickel transport. Data will be collected within the framework of the triple-layer model to allow inclusion of these effects in the Ni transport calculations with the LEHGC version of the HYDROGEOCHEM code[9]. Sorption data will also be collected and analysed within the framework of ion-exchange theory. Ion-exchange experiments will be carried out for Ni-Na, Ni-Li and Li-Na exchange. Values of the ion-exchange equilibrium constants will be calculated and the robustness of the ion-exchange model will be compared to that of the isotherm model for lithium and that of the TLM model for nickel.

V. SUMMARY

The geochemical properties of a porous sand and several tracers (Ni, Br, and Li) have been characterized in order to design a caisson experiment for validation of reactive transport models. The geochemical data obtained in preliminary characterization studies suggest that the range of probable tracer velocities will allow for detection of the tracers at sufficient depths (>100 cm) for modeling and within relatively short (<6 months) breakthrough times. Based on the studies described in this paper, the following geochemical parameter values were used for the purposes of caisson design:

Influent Ni tracer concentrations:	100	ng/ml
Expected range of Ni K_d:	15 - 90	ml/g
Influent Li concentration:	10	μg/g
Expected Li K_d:	0.2	ml/g
Influent Br concentration:	[illegible]5	μg/g
Expected Br Kd value:	0	ml/g

The surfaces of the sand grains have been characterized by a combination of techniques including potentiometric titration, acid leaching, optical microscopy, and scanning electron microscopy with energy-dispersive spectroscopy. Although the bulk chemistry and mineralogy suggest that the sand is predominately quartz, the surface studies indicate the presence of non-trivial amounts of carbonate, kaolinite and and iron-oxyhydroxides. It is proposed that the chemical composition of pore fluids within the caisson will be controlled by dissolution of quartz, carbonate cement, diffusion of atmospheric CO_2 into pore fluids, hydrolysis of silanol (SiOH) groups and hydrolysis of FeOOH surface groups. It is anticipated that chemical conditions within the caisson will initially be transient but that a steady-state chemical profile may eventually develop.

The experimental data suggest that a linear (K_d) or an isotherm sorption model may adequately describe transport of Li. The sharp pH-dependent sorption edge for nickel suggests that a model describing the changes of pH and the concentrations of other solution species as a function of time and position within the caisson, and the concomitant effects on Ni sorption may be required for accurate predictions of nickel transport. The results of future experiments will be interpreted under the formalisms of linear sorption (K_d's), non-linear sorption, ion exchange, and the triple-layer model. The different approaches will be used to simulate transport of the tracers in the caisson; the validities of the sorption models for the conditions of the caisson experiment will be evaluated by comparing predicted and measured elution curves.

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APPENDIX A. SORPTION OF TRACERS BY SOLUTION SAMPLERS AND PLASTIC LABWARE

A. Sorption on Plastics Containers

Ni sorption on several plastics (low-density polyethylene (LDPE), polypropylene (PP), polyallomar (PA), and polycarbonate (PC)) has been investigated as a function of pH in two studies. In the first, which simulated static storage of raw samples, two batches of effluent from a Wedron 510 sand column were spiked with 5 or 50 ng/m*l* Ni, and aliquots were equilibrated for two days in LDPE bottles (both new and acid-washed). Although the effluent contained either 1.0 or 4.6 ng/m*l* Ni, partially obscuring experimental effects, it appears that some concentration-dependent sorption occurred, amounting to 7% and 3% at final Ni concentrations of 5 - 10 ng/m*l* and 45 - 50 ng/m*l*, respectively.

In the second study, which was designed to maximize the effect of any sorption phenomena, small aliquots of 0.01 *M* NaCl containing either 5 or 50 ng/m*l* Ni were equilibrated in large containers for nine days with continuous agitation. Container materials included PP, PA, and PC, and solution pH was adjusted to cover the range 5–9. Results are plotted in Fig. 4. No sorption was evident for PP and PA containers for pH < 6; sorption increased steadily with increasing pH and exceeded 80% at pH 9.5. The proportion sorbed was independent of initial concentration for the two values tested. The PC containers sorbed significant amounts of Ni at pH>5; but, the relationship between sorption and pH was obscured by leaching of an acidic component from the container walls and incomplete sorption equilibrium.

Desorption was investigated by acidifying the equilibrated samples to 1% HNO_3, re-equilibrating for five days with continuous agitation, and then comparing the final with the initial Ni concentrations. Sorption appears to be fully reversible for samples originally at pH 8 or less before acidification. At higher original pH values, the data are equivocal, with significantly higher final than initial Ni concentrations, most likely the result of contamination problems.

It appears that each of the plastics becomes a significant sorber of Ni under neutral and alkaline conditions, and may have to be accounted for in future sorption experiments and tests of Ni solubility. These studies indicate that all of the plastics are suitable for use as geochemical sampling vessels for acidified solutions. Acidification need not be immediate, as Ni is readily stripped from the vessel walls by 1% HNO_3 (this has not yet been strictly verified for LDPE).

B. Sorption of Li, Ni, and Br by Ceramic and Hollow Fiber Samplers

The uptake of tracers by the hollow-fiber dialysis tubing and high-flow ceramic samplers was evaluated. The dialysis tubes were used in a previous caisson experiments.[10] Because of concerns that the tubing will collapse under high extraction suctions, the ceramic cups were also considered for this experiment. Batch sorption tests with the electrodiaylis tubing indicate that the tubing has a leachable acidic component. In these tests, approximately 3 g of tubing was placed in 30 m*l* 0.01 *M* NaCl solution with 50 ppb Ni, 10 ppm Li, and 1 ppm Br and agitated for 1 day. The equilibrium pH was 5.8 and sorption of the tracers was negligible.

Sorption of Ni, Br, and Li onto Soil Moisture B1M3 ceramic samples was measured in batch and flow through experiments. Batch experiments were carried out with a sampler that had been ground to the <200 μm size fraction, and pre-equilibrated for 18 hours in 0.01 *M* NaCl electrolyte in 40 m*l* PC centrifuge tubes. No attempt was made to control the pH; the equilibrium pH was 8.3 at a solution:solid ratio of 9 m*l*/g. Sufficient nickel, bromide, and lithium were added together to the centrifuge tubes to yield initial tracer concentrations of 50 ppb Ni, 10 ppm Li, and 1 ppm Br respectively. The centrifuge tubes were agitated on hematology mixers for 2 days. After the equilibration period, the solutions were separated from the solid by centrifugation (11,000 rpm for 10 minutes). Final tracer concentrations were measured as described previously. The K_d's measured for Ni, Br and Li were 61, -6 and -4 ml/gm respectively. The negative K_d's may indicate leaching of tracers from the ceramic samplers.

Three flow-through experiments were carried out under atmospheric conditions in which 0.01 *M* NaCl solutions with nominal concentrations of 50 ppb Ni, 1 ppm, Li and 7.3 ppm Br were drawn through a B1M3 ceramic sampler at 0.35 ml/min. In the first and second experiments attempts were made to buffer the pH at near neutral and alkaline values with sodium borate buffer (10 or 4 ppm B); in the third experiment, the pH was controlled by atmospheric CO_2 and the properties of the ceramic sampler. In the second and third experiments the pH declined over the course of the experiments due to uptake of CO_2 by the solution. The pH values were 8.8, 7.6 to 7.3 and 7.2 to 6.5 for the first, second and third experiments respectively.

Breakthrough curves for Li and Br from the first experiment are shown in Figure A1. For both elements, breakthrough (defined at $C/C_0 = 100\%$) was achieved after 50 ml of solution had been eluted. The final concentrations were from 5 to 10% higher than those of the feed solutions. This may be due to the effect of evaporation during the time required for analysis or leaching from the ceramic.

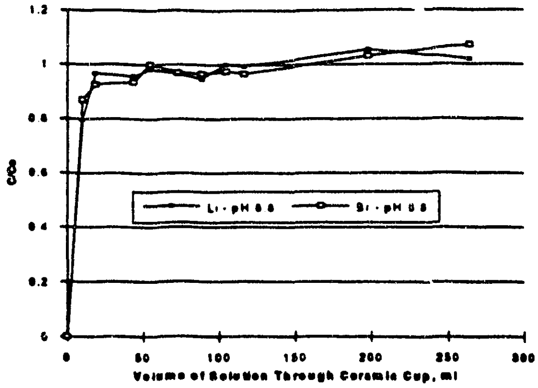

Figure A1. Li and Br breakthrough curves for flow through B1M3 ceramic sampler.

Ni breakthrough curves for pH 6.5 and 7.4 from the second and third experiments are shown in Figure A2. Breakthrough ($C/C_0 = 100\%$) was not reached until approximately 1000 ml of solution had passed through the creamic sampler. The concentration of Ni in the influent reservoir was measured at the end of the experiment and found to be 40 ppb rather than the expected value of 50 ppb. The cause of this discrepancy is unknown but may be due to experimental error or sorption of the Ni by the glass reservoir vessel.

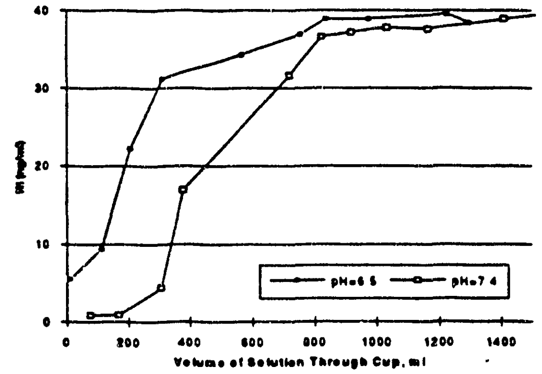

Figure A2. Ni breakthrough curves for flow through B1M3 ceramic sampler.

The results of the batch and flow-through tracer tests indicate that the B1M3 ceramic cups would not be suitable solution samplers for Ni tracer studies. Ni sorption by the electrodialysis tubing is negligible, therefore this material will be used to study Ni migration in the caisson. The batch and flow-through experiments indicate that Br and Li are not sorbed by the ceramic cup; however, there is some evidence that these elements may be leached from this material. Solutions sampled with the ceramic cups will be analysed for Br and Li; in addition, samples obtained with the dialysis tubing will be analysed for these tracers.

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